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A Multi-scale Flow Battery Modeling Approach Using Mass Transfer Coefficients[1]

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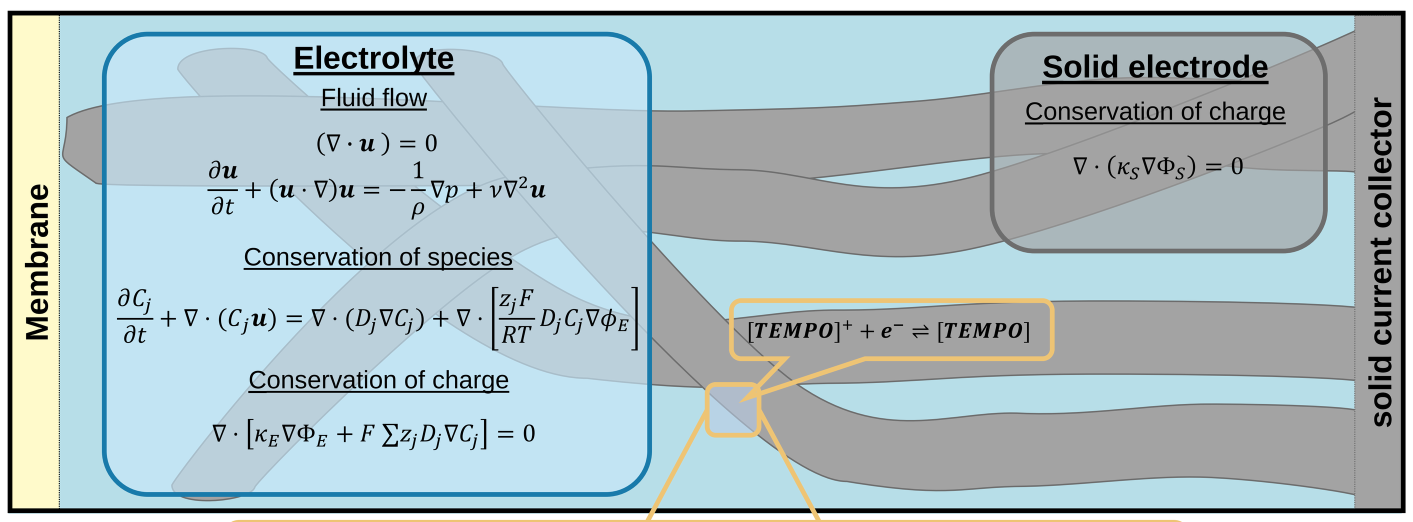
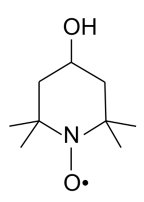
3D Resolved Micro-scale Model [2] (MSM)





Kinetic boundary condition: Butler-Volmer-Type

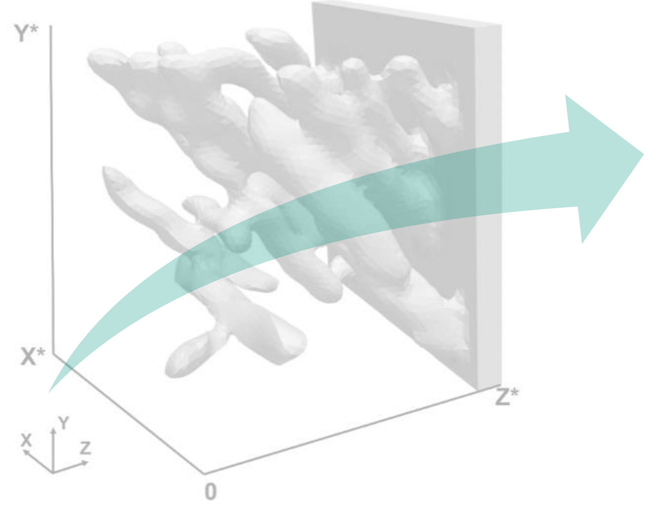
$$-r_{T^+} = +r_T = k \cdot (C_T^s)^{\alpha} \cdot (C_{T^+}^s)^{(1-\alpha)}\left[exp\left(\frac{(1-\alpha)F\eta}{RT}\right) - exp\left(-\frac{\alpha F \eta}{RT}\right)\right]$$

$$\eta = \Phi_S - \Phi_E - E^0 - \frac{RT}{F}\ln\left(\frac{C_{T^+}^s}{C_T^s}\right)$$

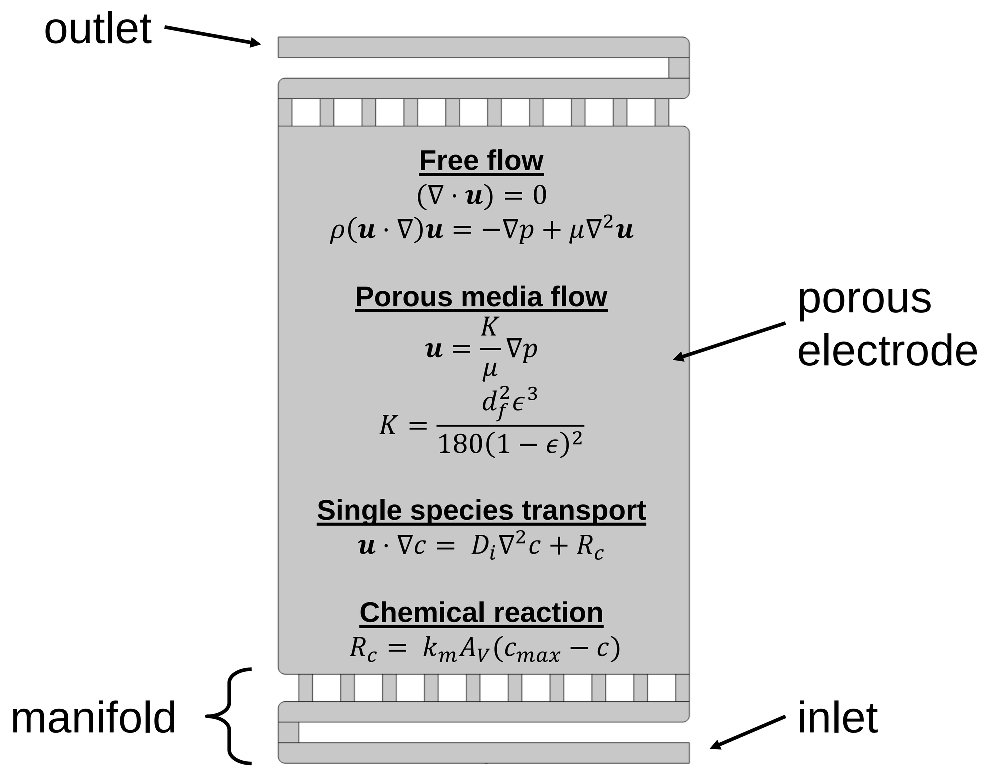
$$r = \frac{i}{F}$$

2D Homogenized Cell Scale Model (HCSM)

$$k_m = \frac{r}{c_{bulk} - c_{surf}}$$



$$N_c = k_m A\left(c_{bulk} - c_{surf}\right)$$



Motivation

Vague description of the mass transfer coefficient k_m in homogenized cell scale models. Mostly as empirical relation to velocity.

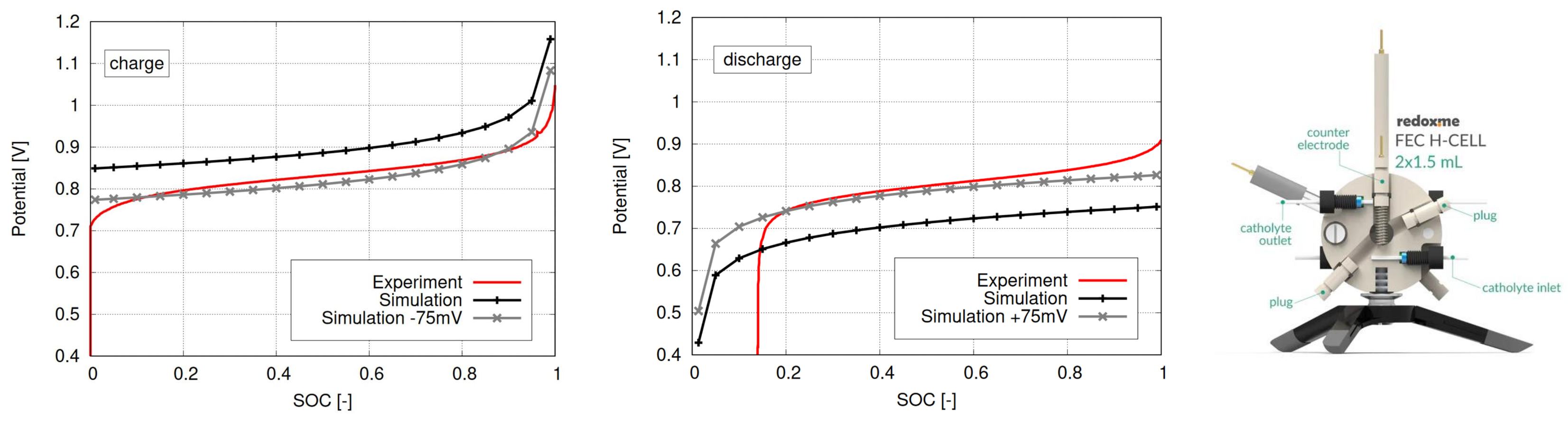
Research Objective

Development of a method to extract k_m from MSM and subsequent usage in the HCSM. Comparison to empirical relations from literature.

Approach

Obtainment by using reaction rate at distinct concentration level and discharge rate of the MSM, as well as resolved of bulk and surface concentration. Implementation of k_m in the HSCM as function of SOC and velocity.

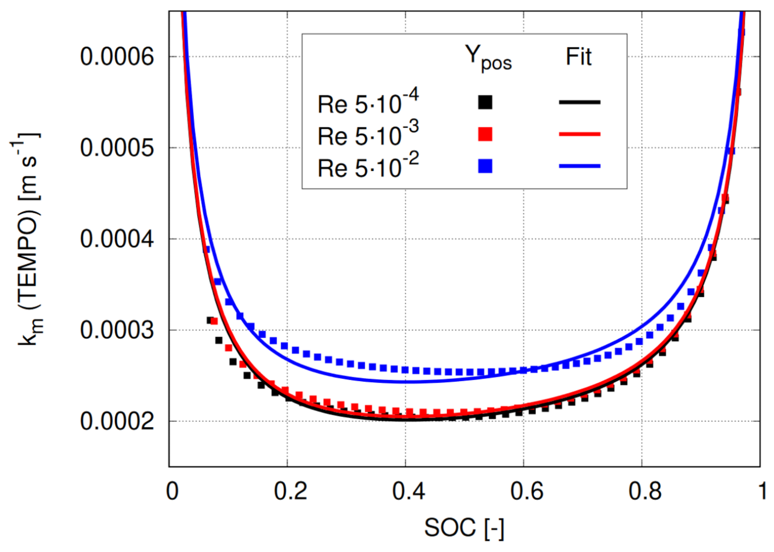
Experimental Validation of the MSM



Potential vs SOC for the first charge (left) and first discharge (right) cycle of the *redoxme* FEC H-Cell. Independent measurements of half-cell potentials. The current density is 2.83 mA cm^{-2}, the concentration is 0.011 M TEMPO in 1 M NaCl and the flow rate is 30 mL min^{-1} (0.0177 m s^{-1}).

The experiment is marked in red, simulation results are colored in black. To fit the experimental results, the simulated potential is modified with 75 mV (gray) arising from membrane polarization.

MSM mass transfer coefficient extraction

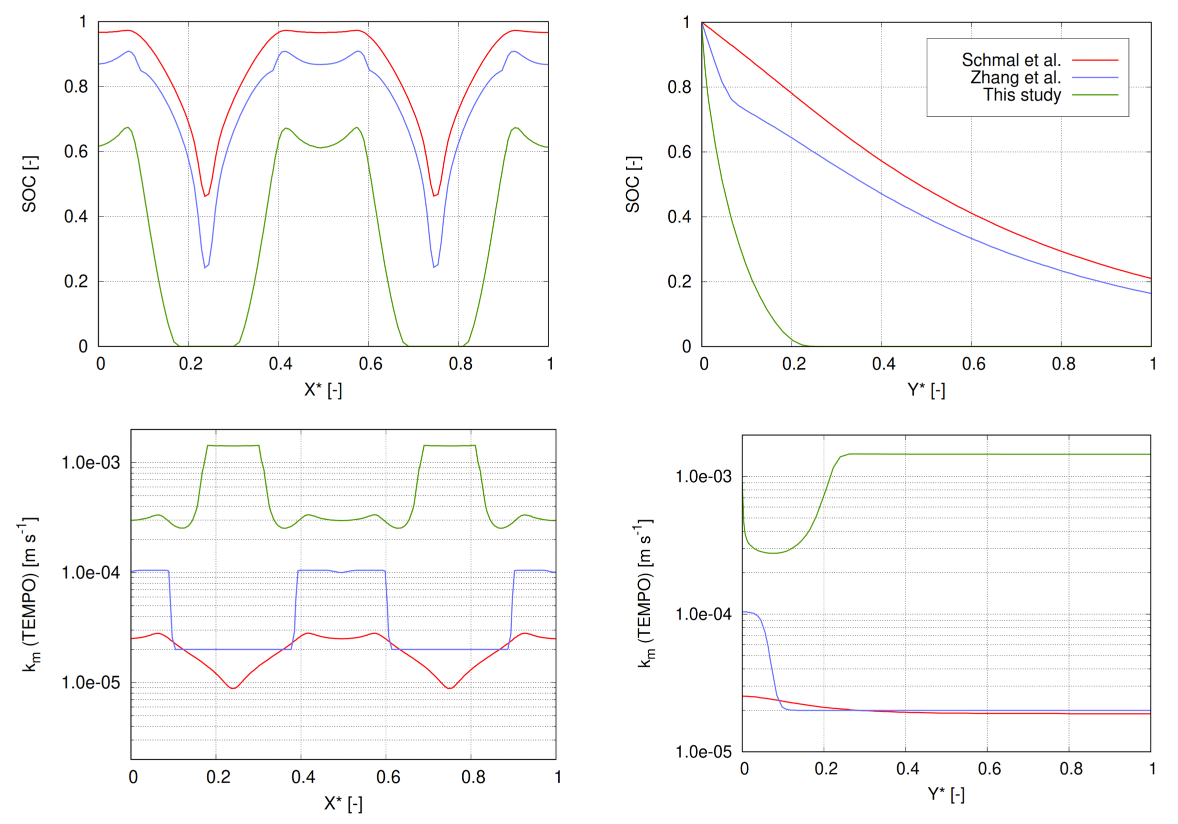


$$k_m = c + d \cdot U + \frac{b}{\sin\left(\pi a\left(SOC + 0.5\left(\frac{1}{a} - 1\right)\right)\right)} + e \cdot SOC$$

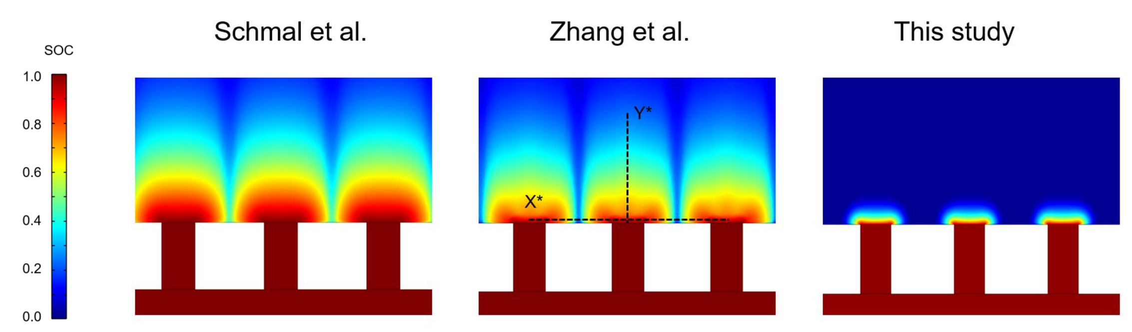
Parameter	Value	Unit
a	0.9695	-
b	6.241 × 10^{-5}	m s^{-1}
c	1.114 × 10^{-4}	m s^{-1}
d	8.425 × 10^{-3}	-
e	6.036 × 10^{-5}	m s^{-1}

Extracted mass transfer coefficient as function of velocity and SOC (squares) and the corresponding fitting function (line). The initial concentration is 0.1 M TEMPO in 1 M NaCl and the discharge current density is 80 mA m^{-2}. Root mean square error between data and fit is 2.45×10^{-5}. The fit is conducted to be finite at the SOC boundaries.

Comparison of mass transfer coefficients



Comparison of different mass transfer coefficient approaches and their respective SOC. Horizontal (X*) and vertical (Y*) cut line within the electrode directly after the inlet manifold. The inlet flow rate is 70 mL min^{-1} which ensures a flow regime corresponding to Re ~ 5×10^{-2}. Operating conditions are set to fit the discharge conditions of the coefficient extraction. Excerpt of the inlet manifold for qualitative comparison (below).



Schmal et al.[3] $k_m = 1.6 \times 10^{-4}\,|\boldsymbol{u}|^{0.4}$

Zhang et al.[4] $k_m = \left(\left(1 + exp\left(-4665\,\frac{u}{1\,ms^{-1}} + 42.302\right)\right)^{-1} + 0.235\right) \cdot 8.511 \times 10^{-5} \cdot 1\,ms^{-1}$

References

[1] Wolf, A., Baudrin, E., Nirschl, H., (2023) Energy Technology. https://doi.org/10.1002/ente.202300175

[2] A. Wolf, S. Kespe, and H. Nirschl. John Wiley & Sons, Ltd, 2023. Chap. 18, pp. 413–442. doi: https://doi.org/10.1002/9783527832767.ch18.

[3] D. Schmal, J. Van Erkel, and P. J. Van Duin. Journal of Applied Electrochemistry 16.3 (May 1986), pp. 422–430. doi: 10.1007/BF01008853.

[4] D. Zhang et al. Journal of Power Sources 447 (2020), p. 227249. doi: https://doi.org/10.1016/j.jpowsour.2019.227249.

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